PATENT SPECIFICATION

1,044,502

NO DRAWINGS **1,044,502**

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COMPLETE SPECIFICATION

Stretched Polyolefin Compositions

We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7, Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the stretching of filled polyolefin compositions, and is an improvement in or modification of the invention disclosed in our Specification No. 29386/63.

The use of inorganic fillers as extenders and/or reinforcing agents for rubbers and some other resins is well established. Most attempts to use fillers in a similar manner to extend and/or reinforce the more crystalline polyolefins, however, have met with failure, brittle products generally being obtained even with moderate filler concentrations. Previous attempts have been made to produce poly (*alpha*-olefins) filler blends using conventional inert fillers alone, and although occasionally these blends are found to have greater tensile strength than the unfilled polymer, most of them are too brittle to be useful as general purpose resin-base compositions. On the whole, reported studies of poly (*alpha*-olefin)/filler blends indicate that satisfactory products are rarely obtained. Small amounts of some inorganic materials can be blended into poly (alpha-olefins) as pigments, but in amounts too small to serve other purposes.

Fillers are now widely used as extenders for glass fibre reinforced resins. In most cases of this type, the filler does not impart any reinforcement, but does have a favourable effect on cost, shrinkage, thermal effects, surface properties, and flow properties. However, apparently no other material is reinforced by fillers to the same extent as the natural or synthetic rubbers.

In Specification No. 29386/63 (Serial No. 1,044,028) we have disclosed polyolefine compositions which unexpectedly retain a substantial proportion of the flexibility, impact resistance and strength of the base polymers, said compositions comprising a three component system consisting of (i) a polyolefin of molecular weight sufficiently high to give it a standard load melt index of substantially zero (ii) an inert filler material, and (iii) plasticiser. We have also disclosed that the compositions can be processed by extrusion, injection moulding, vacuum forming, or calendering, and that cold pressing produces changes in properties that are desirable under some circumstances. A wide variety of articles such as films, sheets and other shaped articles can be produced from the blends, and the articles can be rendered porous if desired, by removing part or all of the filler, plasticiser or both by solvent extraction, using either aqueous or organic solvents, depending on the particular fillers and plasticisers used.

Such blends have a wide variety of uses and are particularly advantageous because of their relatively low cost. Compositions having a high concentration of plasticiser are of particular interest because of the low cost of plasticiser and the increased workability it imparts to the blend. While high filler concentrations eliminate disadvantageous plasticiser exudation under normal conditions, for some uses of the material, particularly at elevated temperatures, the exudation of the plasticiser has been found to be too great.

According to the present invention, a sheet (as hereinafter defined) or filament is formed from a homogeneous blend comprising 10—80% by volume of a crystalline poly (*alpha*-olefin) having a standard load melt index, as specified in ASTMD 1238—52T, of substantially zero, the *alpha*-olefin having from 2—4 carbon atoms, 5—60% by volume of inert particulate filler material, and 15—85% by

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volume of plasticiser which is defined as a material that lowers the melt viscosity, improves the flexibility of the final composition and aids the production of porous objects, at a temperature above the coalescing temperature of the blend, and the size of the sheet in at least one direction parallel to its surface is increased, or the length of the filament is increased, by at least 5%, preferably at least 10%, by stretching.

We have found that the rate of exudation of plasticiser from such blends is decreased thereby.

The term "sheet" is employed herein to denote not only thin films, tapes and substantially uniplanar sheets, but also sheets which are in the form of a three-dimensional structure, i.e. curved sheets and also tubes which can be regarded as sheets which are curved into a cylindrical or other closed form.

The sheets and filaments may be stretched at temperatures either above or below the softening temperature of the blend, temperatures below the softening temperature of the blends being desirable if increased strength is desired, and temperatures above the softening temperature if polymer crystal orientation is to be avoided and if greater elongation is desired. Filaments will normally be stretched in boiling water or in saturated steam, e.g. above boiling water, at atmospheric pressure.

Extruded or calender produced sheets and extruded filaments may be formed from the blends by conventional methods. The composition is generally introduced into the processing equipment in the form of pellets. The particular process temperatures and other conditions which provide the optimum results differ somewhat from blend to blend, but determination of such factors is a matter of mere routine experiment. Such sheets and filaments may be stretched in accordance with the invention by any conventional methods. Typical methods and apparatus for stretching sheets are described in United States Patent Nos. 2,995,779 and 3,078,504, for example. The stretching can be obtained by moulding the sheet by matched mould forming, slip forming, vacuum forming, or air blowing sheets of the composition at temperatures below or above the coalescing temperature by conventional techniques such as those shown and described in Chapter 8 of " Processing of Thermoplastic Materials" by Ernest C. Bernhardt (1959).

The desired stretching may also be obtained in the course of the formation of the " sheet," for example by forming a film from an extruded tube by a method such as that described in United States Patent No. 2,763,029 and Chapter 20 of " Polyethylene, the Technology and Uses of Ethylene Polymers," edited by Renfrew and Morgan (1957).

This method generally involves the extrusion of a continuous tube, as above described, and the introduction of gas, normally air, under presssure into the tube. The gas expands the uncooled tube into a tubular film which then may be cooled by air currents or by cooled rollers.

The poly (*alpha*-olefin) component may comprise one or more of the following crystalline polyolefins: high density polyethylene, low density polyethylene, polypropylene, ethylenebutene copolymer, poly (butene-1), propylene-(butene-1) copolymer and ethylene-propylene copolymer.

Preferred water-insoluble fillers include kaolin, calcium silicate, calcium carbonate, magnesium carbonate, magnesium oxide, stannic oxide, mica, glass beads, glass flakes, asbestos, carbon black, silica, aluminium polysilicate, montmorillonite, attapulgite, talc, wood flock, and mixtures thereof. However, any finely divided material which retains its particulate characteristics under the processing conditions may be suitable and the following classes of compounds may be cited by way of example.

(a) Carbon blacks, coal dust, graphite,

(b) Metal oxides and hydroxides, especially those of silicon, aluminium, calcium, magnesium, barium, titanium, iron, zinc, tin,

(c) Metal carbonates, especially those of calcium, magnesium, sodium and potassium,

(d) Metal silicates and aluminates; naturally occurring clays such as montmorillonite, kaolin, attapulgite, asbestos, mica, muscovite, talc, vermiculite; precipitated silicates, synthetic and natural zeolites, portland cement, calcium silicate, aluminium polysilicate, alumina silica gels,

(e) Meals such as aluminium, lead,

(f) Polymers such as nylon, and phenol formaldehyde resins,

g) Wood flour, fibres and bark products,

(h) Glass particles such as microbeads, hollow microspheres, flake, fibre,

(i) Miscellaneous materials such as molybdenum disulphide, zinc sulphide.

Preferred water-soluble fillers include sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, calcium acetate, copper acetate, barium acetate, sodium sulphate, potassium sulphate, sodium phosphate, potassium phosphate, sodium nitrate, potassium nitrate, sugar and mixtures thereof.

Preferred water-insoluble plasticisers include petroleum oils, petroleum waxes, butyl stearate, dibutyl sebacate, dioctyl sebacate, ethylene-vinyl acetate copolymer, polyisobutylene, diisodecyl phthalate, dioctyl fumerate, asphalt, polyester-glycol, octyl epoxy tallate, chlorinated biphenyl and mixtures thereof. The following illustrative types of compounds are also suitable:

(a) Esters, e.g. sabacates, fumarates, phthalates, stearates, adipates, citrates, etc.; epoxy compounds; polyesters.

(b) Phosphate esters.

(c) Hydrocarbons-petroleum oils, waxes, resins, asphalt and these materials containing oxygen, nitrogen, and sulphur groups, blown asphalt; pure compounds such eicosane, low molecular weight polymers such as polyisobutylene, polybutadiene, hydrocarbon resins, polystyrene and homolog copolymers of styrene, poly (*alpha*-methyl styrene), atactic polypropylene, ethylenepropylene copolymer and other rubbers, ethylene-vinyl acetate copolymer, oxidized polyethylene, coumarone-indene resins, terpene resins,

(d) Chlorinated hydrocarbons including oils and waxes.

(e) Miscellaneous plasticisers — sulphonamide, coumarone-indene, laurone, tall oil, drying oils such as linseed oil.

Preferred water-soluble plasticisers include glycol, glycol ethers and esters, glycerin, glycerol monoacetate, diethylene glycol, diethylene glycol ethers and esters, triethylene glycol, polyethylene glycol (molecular weight of about 400—20,000), propylene glycol, diisopropylene glycol, polypropylene glycol (molecular weight of about 260—1200), trimethylene glycol, tetramethylene glycol, 2,3-butylene glycol, triethyl phosphate, polyvinyl alcohol, partially hydrolized polyvinyl acetate, polyacrylic acid, polyvinyl pyrrolidone and mixtures thereof.

The general considerations affecting the choice and use of the plasticisers and fillers are discussed in Specification No. 29386/63 (Serial No. 1,044,028). It is particularly to be noted, however, that all combinations of water-soluble and water-insoluble fillers and plasticisers may be used and that part or all of the filler, plastiser or both may be removed by solvent extraction from shaped articles formed from the blends to render the articles porous.

It is also to be noted that up to 85% by volume of the polyethylene, or other polyolefin of melt index substantially zero may be replaced by polyethylene, for example, having a melt index of 0.1 or greater.

A particularly suitable composition is a homogeneous blend of a poly (*alpha*-olefin) having a standard load melt index of substantially zero containing 30—75 percent by volume of plasticiser and 10—55 percent by volume of filler.

Examples of extruded, stretched filaments in accordance with the invention are shown in Table I.

The stretched filaments suffered greatly decreased plasticiser exudation with respect to the basic composition.

A similar result is obtained with the other blends disclosed.

TABLE I

Physical Properties of Extruded, Drawn Filaments

Sample No.	Composition, % by Volume			Drawing Ratio	Tensile Strength g/denier	Elongation at Yield Point %	Knot Tension Strength, g/d:	Knot Elongation at Yield Pt. %	Modulus	
	Polymer	Filler	Plasticiser						g/d	psi
1	Grex-4 40	HR 25 EFT 5	SF412 30	6:1	1.30	11	0.97	9	—	—
2	Grex-4 40	HR 27.5 EFT 2.5	SF412 30	6:1	1.42	11	1.12	8	—	—
3	Grex-4 45	HR 27.5	SF412 25	6:1	1.62	16	1.00	9	13.9	212,000

Grex-4: A particle formed polyethylene sold by W. R. Grace & Co., under the designation FF—60—018 having a S. L. M. I. of 0.0 and a H. L. M. I. (High Load Melt Index) of 1.8, a specific gravity of 0.945 and RSV (Reduced Standard Viscosity) of 4.5

HR An aluminium silicate (kaolinite) sold by Georgia Kaolin Co., under the name Hydrite R and of average particle size 0.77 microns.

EFT : A carbon black sold by Cabot Corp. under the name Eltex.

SF412: A plasticiser sold by Shell Oil Co. under the name Shellflex 412 comprising 50% paraffinic carbon, 43% naphthenic carbon and 7% aromatic carbon, and having a viscosity of 559 Seconds, Saybolt Universal at 100°F. and 56 Seconds, Saybolt Universal at 210°F.

Table II shows the physical properties of extruded, blown film obtained by the method referred to earlier.

The films were observed to have a dry surface on cooling, whereas tubes (unstretched) made from the same compositions had oily surfaces after cooling.

A similar result is obtained with the other blends disclosed.

Similar results are obtained by stretching the films by other forming techniques, such as vacuum forming at temperatures either below or above the softening points of the compositions. In both instances, a very marked decrease in plasticiser exudution is obtained. Examples of porous films obtained by extracting the plasticiser from films formed by extrusion blowing are shown in Table III. A similar result was obtained by extracting plasticisers and/or fillers from the other blends disclosed.

TABLE II

Physical Properties of Extruded, Blown Film

Sample No.	Composition, Volume %						Density	Tear Resistance gm./mil.	Spencer Impact psi
	Polymer		Filler		Plasticiser				
4	Grex-4	40	HR	30	SF412	30	1.418	14.8	0.250
5	Grex-4	40	HR EFT	25 5	SF412	30	1.347	24.9	0.143
6	Grex-4	40	HR	30	SF412	30	1.190	20.15	0.209
7	Grex-4	40	HR	30	SF412	30	1.418	14.8	0.250

TABLE II (cont.)

Physical Properties of Extruded, Blown Film

Sample No.	Tensile Modulus psi.	Tensile Strength psi.	Stress at Yield Point psi.	Elongation at Yield Point %	Elongation at Failure %
4	127,000	MD(1) 1520 PD(2) 1280	MD 1512 PD 1277	50	400
5	81,000	MD 840 PD 720	MD 638 PD 787	12	730
6	52,500	MD 2840	(3)	(3)	264
7	127,700	MD 1518	MD 1512	MD 50	400

(1) — Machine direction on sheet.
(2) — Perpendicular to machine direction on sheet.
(3) — No yield point observed.

TABLE III

Composition(1)	
Polymer, Vol. %	Grex-4 40
Filler, Vol. %	H121 30
Plasticiser, Vol. %	SF412 30
Tensile Modulus	
MD (Direction of Formation)	227,000
PMD (Perpendicular to MD)	119,000
Stress at Yield Point, psi.	
MD	1,640
PMD	1,000
Elongation at Yield Point %	
MD	112
PMD	4.3
Elongation at Failure, %	
MD	180
PMD	8.8
Tensile Strength, psi.	
MD	1,610
PMD	910
Oxygen Permeability	
cc. mil/atm. m^2 day	182.9×10^3
Water Vapour Permeability	
g.mm./cm. Hg m^2 day	14.34

(1) Subjected to solvent extraction using petroleum ether.

H121 An aluminium silicate (kaolinite) sold by Georgia Kaolin Co. under the name Hydrite 121 and of average particle size 1.5 microns.

WHAT WE CLAIM IS:—

1. A method of obtaining sheets (as hereinbefore defined) and filaments, which comprises forming a homogeneous blend comprising 10—80% by volume of a crystalline poly (*alpha*-olefin) having a standard load melt index of substantially zero, the *alpha*-olefin having from 2 to 4 carbon atoms, 5—60% by volume of inert particulate filler material, and 15—85% by volume of plasticiser, as hereinbefore defined, into a sheet or filament at a temperature above the coalescing temperature, and increasing the size of the sheet in at least one direction parallel to its surface, or increasing the length of the filament, by at least 5% by stretching.

2. A method according to claim 1, wherein the size of the sheet in at least one direction parallel to its surface, or the length of the filament, is increased by at least 10%.

3. A method according to claim 1 or 2, wherein the sheet or filament is stretched at a temperature above the softening temperature of the blend.

4. A method according to claim 1 or 2, wherein the sheet or filament is cooled to a temperature below the softening temperature of the blend prior to stretching.

5. A method according to claim 1 or 2, wherein the filament is stretched in hot water.

6. A method according to claim 1 or 2, wherein the filament is stretched in saturated steam.

7. A method according to any one of claims 1—4, wherein the sheet is stretched by vacuum forming, matched mould forming, slip forming or air blowing.

8. A method according to any one of claims 1—4, wherein the blend is extruded in the form of a tube at a temperature above the coalescing temperature, and the tube is expanded into a stretched tubular sheet by means of gas introduced into the tube under pressure.

9. A method according to claim 8, wherein the gas is air.

10. A method according to any one of the preceding claims, wherein the poly (*alpha*-olefin) component comprises one or more of the following crystalline polyolefins: high density polyethylene, low density polyethylene, polypropylene and ethylene-butene copolymer.

11. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-insoluble fillers: kaolin, calcium silcate, calcium carbonate, magnesium carbonate, magnesium oxide, stannic oxide, mica, glass beads, glass flakes, asbestos, carbon black, silica, aluminium polysilicate, montmorillonite, attapulgite, talc and wood flock.

12. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-soluble fillers: sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, calcium acetate, copper acetate, barium acetate, sodium sulphate, potassium sulphate, sodium phosphate, potassium phosphate, sodium nitrate, potassium nitrate and sugar.

13. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-insoluble plasticisers: petroleum oils, petroleum waxes, butyl stearate, dibutyl sebacate, dioctyl sebacate, ethylene-vinyl acetate copolymer, polyisobutylene, diisodecyl phthalate, dioctyl fumarate, asphalt, polyester-glycol, octyl epoxy tallate and chlorinated biphenyl.

14. A method according to any one of the preceding claims, wherein the blend contains one or more of the following water-soluble plasticisers: glycol, a glycol ether or ester, glycerin, glycerol monoacetate, diethylene glycol, a diethylene glycol ether or ester, triethylene glycol, polyethylene glycol (molecular weight of about 400—20,000), propylene glycol diisopropylene glycol, polypropylene glycol (molecular weight of about 260—1200), trimethylene glycol, tetramethylene glycol, 2,3,-butylene glycol, triethyl phosphate, polyvinyl alcohol, partially hydrolized polyvinyl acetate, polyacrylic acid and polyvinyl pyrrolidone.

15. A method according to any one of the preceding claims, wherein the homogeneous blend of the poly (*alpha*-olefin) contains 30—75% by volume of plasticser and 10—55 percent by volume of filler.

16. A method according to any one of the preceding claims, wherein the poly (*alpha*-olefin) is polyethylene.

17. A method according to claim 16, wherein the polyolefin component of the blend comprises 0 to 85% by volume of polyethylene of melt index of 0.1 or greater and 15 to 100% by volume of polyethylene of substantially zero standard load melt index.

18. A method according to any one of the preceding claims, wherein part or all of the filler or plasticiser or both is removed from the stretched filament or sheet by solvent extraction.

19. A method according to claim 1, substantially as hereinbefore described.

20. Sheets and filaments obtained by a method claimed in any one of claims 1—19.

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